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Effect of Glycerol as a Capping Agent on Cds Nanoparticles

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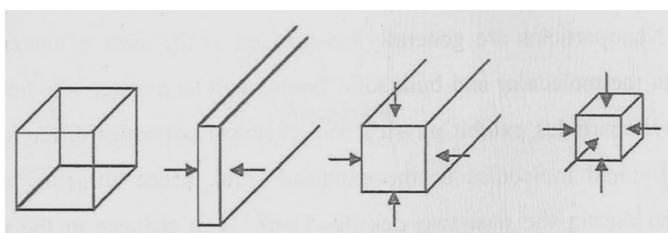
ABSTRACT

Nanoparticles are generally categorized as the class of materials that fall between molecular and bulk solid limits, with an average size between 1-50 nm. Nanoparticles exhibit physical and chemical properties different from either the individual molecules or the extended solid. The changes in the properties of nanoparticles are mainly due to two factors, namely the increase in the surface to volume ratio and drastic changes in the electronic structure of the material due to quantum mechanical effects. For example, while the melting point of bulk CdS is around 1600^0C, a typical 2.5nm CdS crystallite melts at a temperature of about 400^0C.Taking the above properties into consideration, CdS nanoparticles were synthesized using Cadmium Acetate and Thiourea and using Glycerol as a capping agent. The synthesized nanoparticles are characterized by recording the XRD data using (INEL) spectrometer; the sizes are being studied by recording the SEM (model no ss1155).The effective scattering coefficient and the two-photon absorption coefficient are to be estimated. The results indicate that glycerol is not a good capping agent and a better quality of nanoparticles can be obtained if we use thioglycerol as a capping agent.

Keywords: nanomaterials, Cds nanostructures, thioglycerol, capping agent.

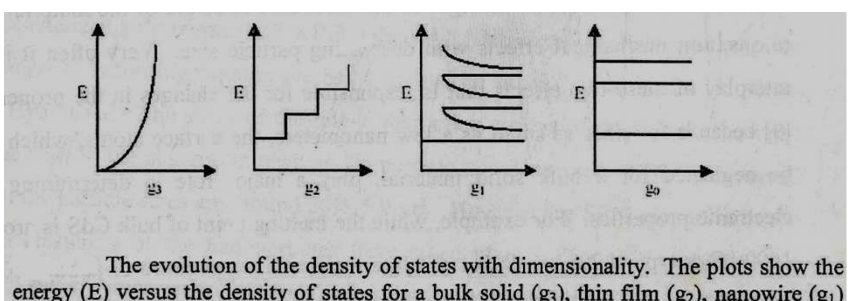
1. INTRODUCTION

Nanoparticles are generally categorized as the class of materials that fall between the molecular and bulk solid limits, with an average size between 1-50 nm. Nanoparticles exhibit physical and chemical properties different from either the individual molecules or the extended solid, hence attracting an enormous attention during the past two decades[1-8]. The changes in the properties of nanoparticles are driven mainly by two factors, namely the increase in the surface to volume ratio and drastic changes in the electronic structure of the material due to quantum mechanical effects with decreasing particle size. Very often it is an interplay of these two effects that is responsible for the changes in the properties[9] because for sizes as small as a few nanometers, the surface atoms, which can be neglected for a bulk solid material, play a major role in determining the electronic properties. For example, while the melting point of bulk CdS is around 1600^0C, a typical 2.5 nm CdS crystallite melts at a temperature of about 400°C[10]. Such a depression in the melting point is due to a higher surface energy of the nanoparticles compared to the bulk. Apart from the effect of a large surface area, the material properties undergo drastic changes in their optical and electronic properties as a function of the size below a certain size regime. Fig. 1.1 schematically shows the density of states for bulk solids compared to those of one, two and three dimensionally confined solids such as in a thin film, in a nanowire and in a quantum dot[4].



Bulk Thin Film Nanowire Quantum Dot

Fig. 1.1



The evolution of the density of states with dimensionality. The plots show the energy (E) versus the density of states for a bulk solid (g_3), thin film (g_2), nanowire (g_1) and quantum dot (g_0).

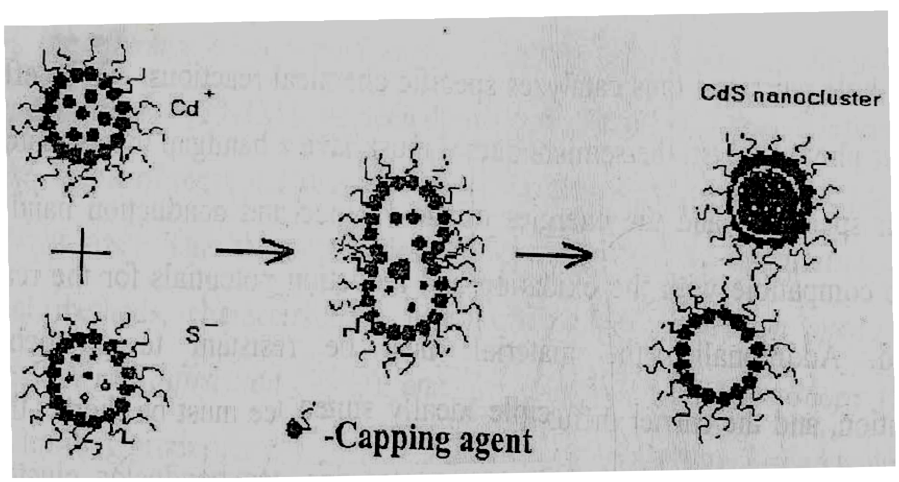
Nanoparticles belong to the quantum dot regime, where the charge carriers are confined to a narrow region along all three directions in space. The physical properties of semi conducting nanoparticles exhibit distinctive changes compared to those of the bulk for sizes below the exciton Bohr radius. An exciton is composed of an electron and a hole. The distance between the electron and the hole within an exciton is called Bohr radius of the exciton. Typical exciton Bohr radius of semiconductors is of a few nanometers.

Nanoclusters

Nanocluster refers to an aggregate of several tens to thousands of atoms or molecules and its grain diameter is about a nanometer. It does not exist in nature and can be obtained only by artificial techniques. Nanoclusters have unique optical, electrical and magnetic properties that are related to the quantum size effect, and the physical properties strongly depend on the number of atoms or molecules.

Capping agent

Capping agent plays a crucial role in the chemical synthesis of nanoparticles. It controls particle size and reduces clustering of particles and aggregation by controlling the reaction as shown in fig. 1.2. Here glycerol is used as capping agent. But according to literature thioglycerol is a better capping agent then glycerol. Here glycerol has been tried in order to obtain large size particles as with glycerol leads to clustering leading to cluster sizes of about 800 nm. This was done with the intension to introduce nonlinear scattering along with the nonlinear absorption.



CD^{+}, S^{-} surrounded by capping agent to control reaction and particle size in the formation of nanoclusters.

Fig.1.2

Semiconductor Nanoclusters

Semiconductor nanoc1usters are of great interest because of their applications as photo catalysts for solar fuel production and solar detoxification.

2. SYNTHESIS SETUP

The figure. 2.1 below describes the experimental set-up used for the synthesis of the CdS nanoclusters. The reaction is carried in the round-bottom flask at 110°C on an oil bath in the nitrogen atmosphere. Water circulator is used to condense the vapors produced during the course of the reaction.

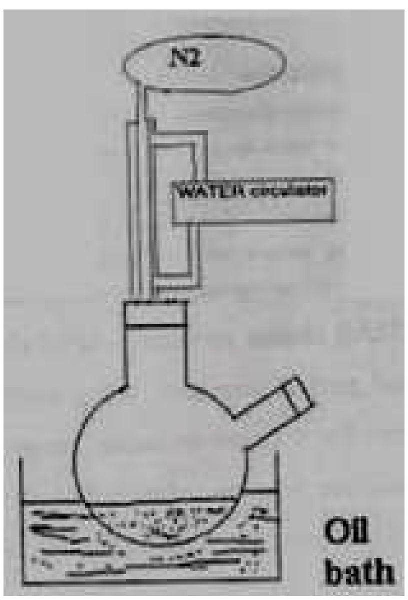


Fig. 2.1 : Experimental setup to chemical synthesis of Cds nanoparticles

Synthesis of CdS

We have synthesized CdS Nanoclusters of different sizes using glycerol as the capping agent. The method followed was similar to that reported by Vossmeyer *et al.*[16], but we used glycerol instead of thioglycerol. In this case 2.35 gm of Cadmium Acetate (10.19 mmol), 0.475 gm of thiourea (6.24 mmol) and 0.64 ml of glycerol (10.95 mmol) in 5ml DMF were taken in a round bottomed flask and heated using oil bath at 110°C for about an hour under nitrogen atmosphere as shown fig. 2.1. This was followed by refluxing the reaction mixture for about 0-16 hours at 150°C. We have followed the method known in the literature as size selected precipitation technique as discussed in the next section.

Size-Selective Precipitation

The method of size-selective precipitation has recently been described in detail[13,14] and was used to isolate the clusters. Acetone was added to our solution until the large particles started to precipitate and are purified by reprecipitation and washing three times with acetone and three times with diethyl ether. We obtained yellow and greenish yellow nanoparticles size is around 3- 5nm (according to XRD). But the particles aggregated forming nanoclusters.

3. GRAPHICAL PLOTS

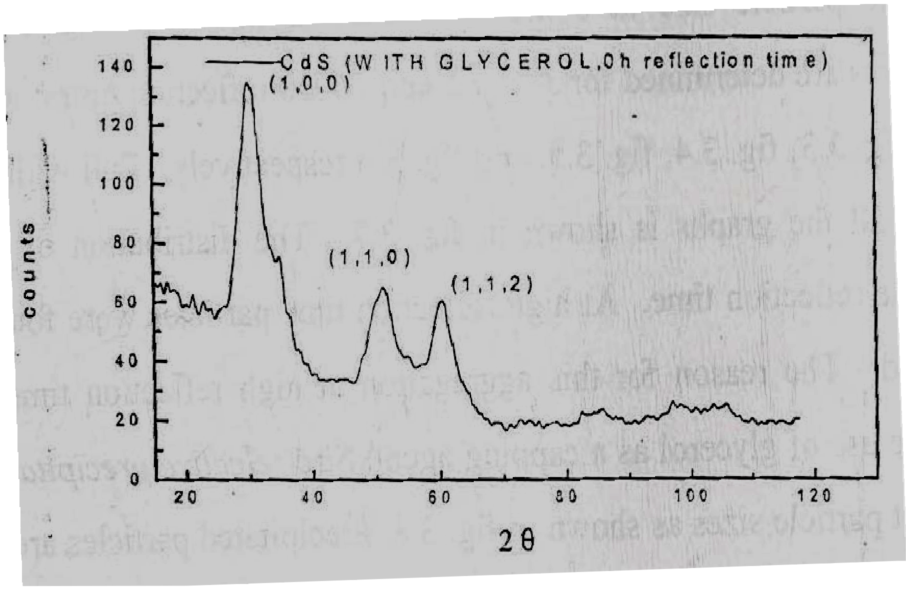


Fig 3.1 : XRD spectra of CdS nanoparticles obtained after *0hours's* reflection time

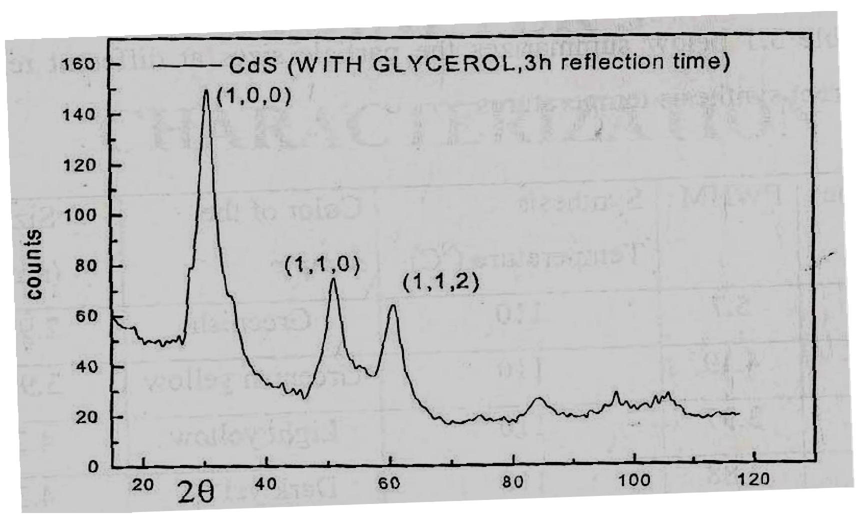


Fig 3.2 : XRD spectra of CdS nanoparticles obtained after *3hours's* reflection time

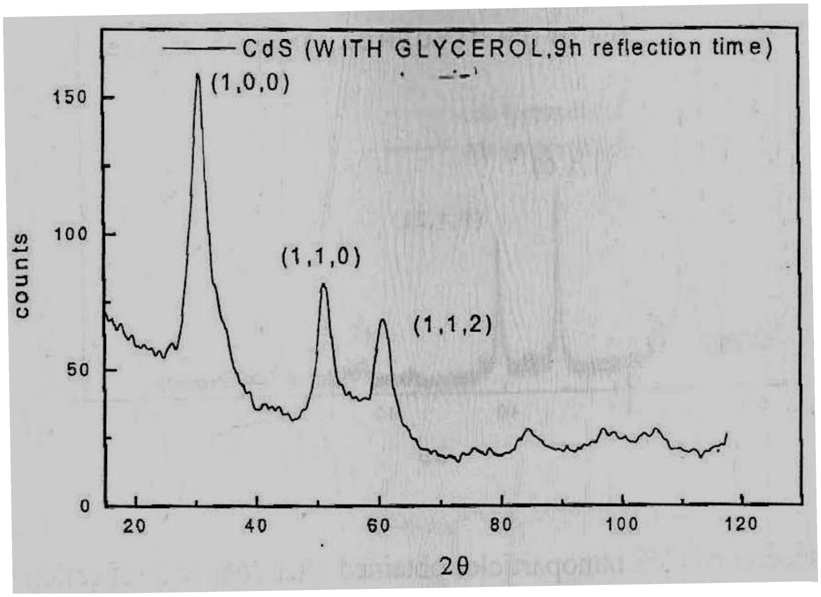


Fig 3.3 : XRD spectra of CdS nanoparticles obtained after *9hours's* reflection time

Particle Size measurements

Nanoparticles size depends on the reflection time, capping agent and also synthesized temperature.
Using Debye-Scherrer formula

$$d = \frac{0.9\,\lambda}{\beta\ Cos\theta}$$

the particle sizes were calculated.

Here

d= diameter of the particle
λ= wavelength of X-ray (Cobalt target $K_{\alpha 1}$=1.78897^{0}A, $K_{\alpha 2}$=1.79285^{0}A, K_{β}=1.62079^{0}A)
β= Full width at half maximum (at 2θ) in X-RD graph
θ=Half of the Bragg angle at maximum peak

XRD Spectra of the samples are taken on INEL X-Ray diffraction spectrometer operates at I=25mA, V=35KV, cobalt target, wavelength λ = 1.78897° *A*. This gives an approximate size of the particle.

Properties of Bulk Cadmium Sulphide (CdS)

Crystallographic properties

- Crystallographic structure: Hexagonal
- a= 0.4135nm, c= 0.6749nm
- Color: Red

Physical properties

- Density: 4.82 g/cm3
- Melting point: 1748 °C

- Hardness: 4 Mohs
- Thermal conductivity: 15.9 W m-I K-1
- Dielectric constant: 8.28 1- C, 8.6411 C
- Band gap (@ 300 ^{0}K): 2.53 eV

Crystalline planes

- Orientation: (100), (110), (111)

4. CONCLUSIONS

In this work the XRD was employed to determine the particle size. In chemical synthesis capping agent plays an important role. The particle size of CdS is found to be 3-6nm.Thus glycerol that is employed in this work can be concluded as a moderate capping agent because it allows cluster formation. Clustering of CdS affected the absorption peak that is around 270nm[8] instead of 370 nm as expected without clusters.

We successfully synthesized CdS nanoparticles and characterized the particles using XRD. The results show that optical non-linear behavior depends on particle size and capping agent.

5. FUTURE SCOPE

Synthesis of nanoparticles and characterization of their optical behavior is one of the most important research topics. The work presented in this paper is just a beginning in the optical characterization of nanoparticles. The synthesis of CdS nanoparticles with thioglycerol as a capping agent can give interesting results, as thioglycerol is a better capping agent as compared to glycerol. A chemical synthesis of nanoparticles is easier than any other method and also gives monodispersive fine particles. More work on nanomaterials synthesis and characterization is proposed to be done in future.

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